



# Analytical Methods Overview

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*The views expressed in this presentation are those of the author(s) and do not necessarily represent the views or policies of the U.S. Environmental Protection Agency.*



# Outline

- Targeted vs. non-targeted
- EPA method categories
- Drinking water (DW)
- Non-DW aqueous samples
- Solids
- Total/absorbable fluorine
- Total oxidizable precursors

**Targeted methods** are methods which are applicable to a specific defined set of known analytes

- Analytical standards exist for quantitation
- Method only 'sees' analytes on the targeted list – will not measure others
- 'One and done' – once the analysis is complete, can't look for other analytes

**Non-targeted methods** involve the use of High-Resolution Mass Spectrometry (HRMS) capable of identifying all analytes in a sample, known and unknown

- Can quantitate those for which laboratory standards exist, otherwise may semi-quantitate based on known, structurally similar analytes
- Can screen for lists of known suspects, can discover new/unknown analytes
- Can store the HRMS data and go back later to look for analytes which were unidentified at the time of analysis, but which later become known



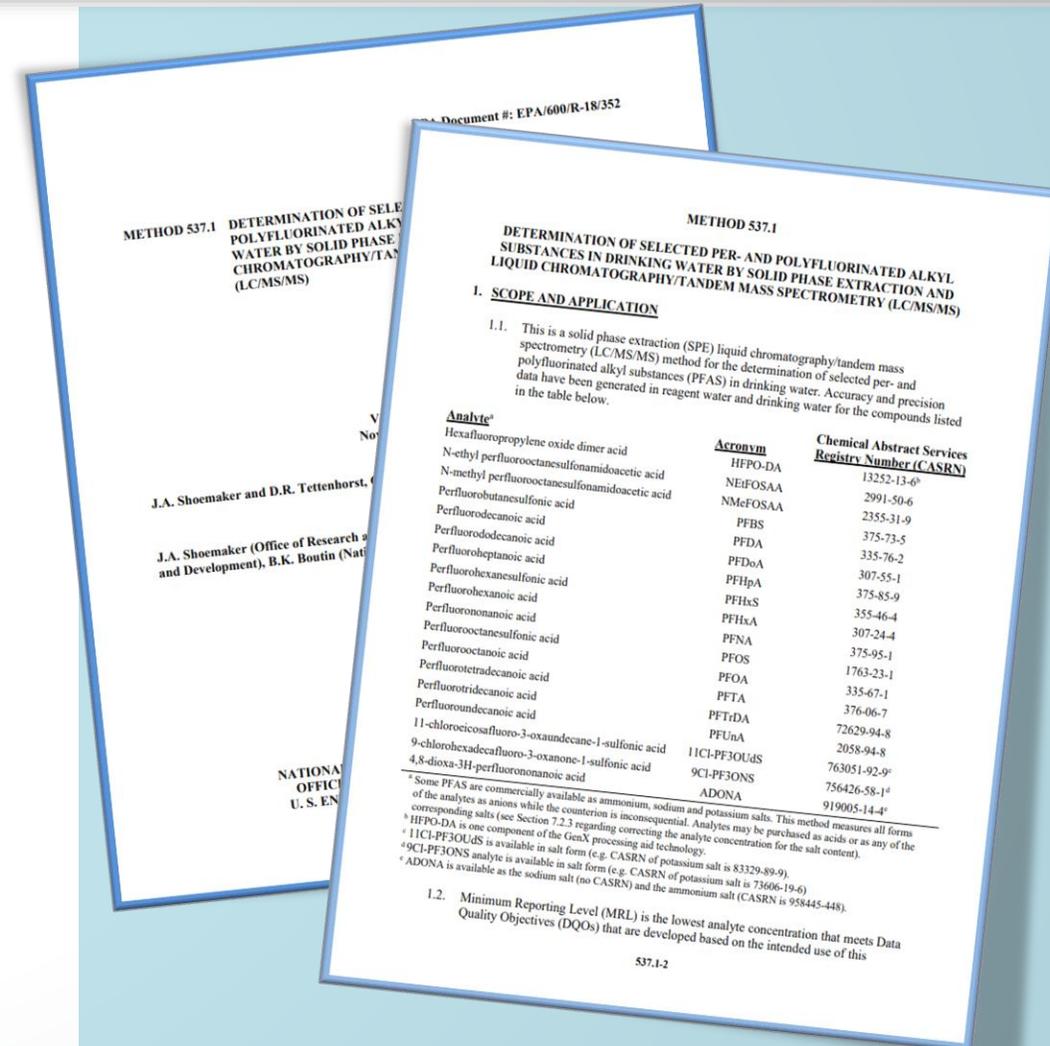
# EPA Method Categories

- Safe Drinking Water Act Methods
  - <https://www.epa.gov/dwanalyticalmethods>
- Clean Water Act Methods
  - <https://www.epa.gov/cwa-methods>
- SW846 Methods
  - <https://www.epa.gov/hw-sw846/guidance-methods-development-and-methods-validation-resource-conservation-and-recovery-act>
- Air Methods
  - Air Emission Measurement Center (EMC)
  - Category A: Methods proposed or promulgated in the Federal Register
  - Category B: Source Category Approved Alternative Methods
  - **Category C: Other Methods**
  - Category D: Historic Conditional Methods (Closed to new method additions)



# Drinking Water Method 537: Revision I

- Update: External lab validation for additional analytes by 537
  - Perfluoro-2-propoxypropanoic acid (GenX chemical HFPO-DA, CAS 13252-13-6)
  - Potassium 9-chlorohexadecafluoro-3-oxanone-1-sulfonate (9Cl-PF3ONS, CAS 73606-19-6)
  - Potassium 11-chloroeicosafluoro-3-oxaundecane-1-sulfonate (11Cl-PF3OUdS, CAS 83329-89-9)
  - Sodium dodecafluoro-3H-4,8-dioxanone (ADONA, CAS 958445-44-8)
- Incorporated clarifications issued in EPA Technical Advisory [epa.gov/sites/production/files/2016-09/documents/pfoa-technical-advisory.pdf](https://epa.gov/sites/production/files/2016-09/documents/pfoa-technical-advisory.pdf)
- Final published method (November, 2018) [epa.gov/water-research/epa-drinking-water-research-methods](https://epa.gov/water-research/epa-drinking-water-research-methods)
- LC/MS/MS with internal standards. Single lab lowest concentration minimum reporting levels (LCMRLs) range from 0.53-6.3 ng/L

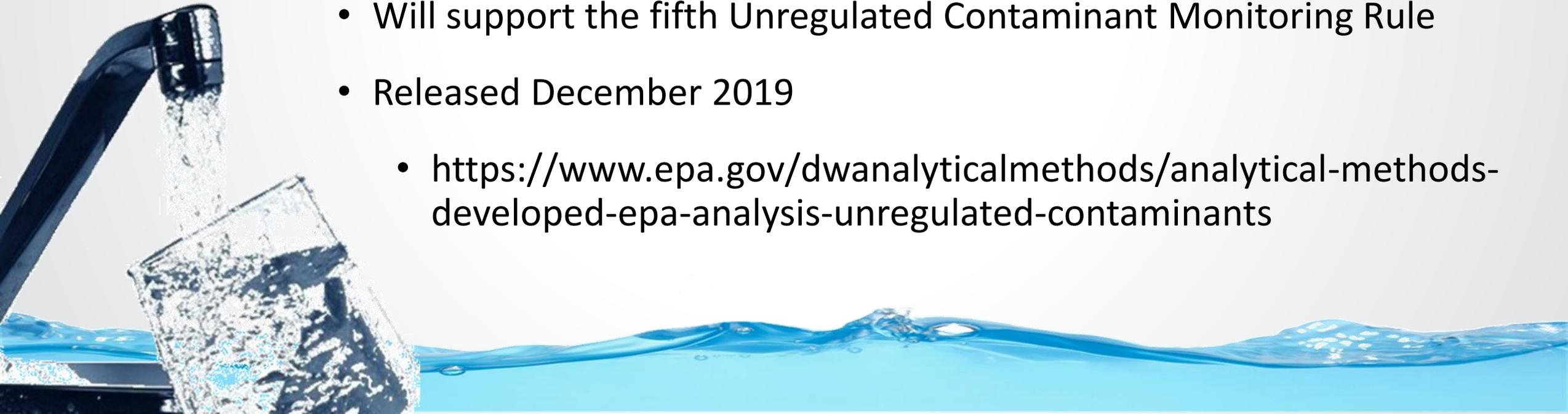




# Drinking Water Method 533

## Solid phase extraction/isotope dilution method targeting PFAS <C12

- Method 537 generally performs poorly for C4 compounds (e.g. PFBA, PFBS)
- Solid phase extraction, LC/MS/MS, Isotope dilution
- Will support the fifth Unregulated Contaminant Monitoring Rule
- Released December 2019
  - <https://www.epa.gov/dwanalyticalmethods/analytical-methods-developed-epa-analysis-unregulated-contaminants>





# DW Methods 533 and 537.1

Method 533	Both Methods	Method 537.1
<b>1H, 1H, 2H, 2H-perfluorodecane sulfonic acid (8:2 FTS)</b>	11-chloroeicosafuoro-3-oxaundecane-1-sulfonic acid (11Cl-PF3OUdS)	N-ethyl perfluorooctanesulfonamidoacetic acid (NEtFOSAA)
<b>1H, 1H, 2H, 2H- perfluorohexane sulfonic acid (4:2 FTS)</b>	9-chlorohexadecafluoro-3-oxanone-1-sulfonic acid (9Cl-PF3ONS)	N-methyl perfluorooctanesulfonamidoacetic acid (NMeFOSAA)
<b>1H, 1H, 2H, 2H-perfluorooctane sulfonic acid (6:2 FTS)</b>	4,8-dioxa-3H-perfluorononanoic acid (ADONA)	Perfluorotetradecanoic acid (PFTA)
<b>Nonafluoro-3,6-dioxaheptanoic acid (NFDHA)</b>	Hexafluoropropylene oxide dimer acid (HFPO-DA)	Perfluorotridecanoic acid (PFTrDA)
<b>Perfluoro (2-ethoxyethane) sulfonic acid (PFEESA)</b>	Perfluorodecanoic acid (PFDA)	
<b>Perfluoro-3-methoxypropanoic acid (PFMPA)</b>	Perfluorododecanoic acid (PFDoA)	
<b>Perfluoro-4-methoxybutanoic acid (PFMBA)</b>	Perfluorohexanoic acid (PFHxA)	
<b>Perfluorobutanoic acid (PFBA)</b>	Perfluoroundecanoic acid (PFUnA)	
<b>Perfluoroheptanesulfonic acid (PFHpS)</b>	<b>Perfluorobutanesulfonic acid (PFBS)</b>	
<b>Perfluoropentanesulfonic acid (PFPeS)</b>	<b>Perfluoroheptanoic acid (PFHpA)</b>	
<b>Perfluoropentanoic acid (PFPeA)</b>	<b>Perfluorohexanesulfonic acid (PFHxS)</b>	
	<b>Perfluorononanoic acid (PFNA)</b>	
	<b>Perfluorooctanoic acid (PFOA)</b>	
	<b>Perfluorooctanesulfonic acid (PFOS)</b>	

Bold indicates analytes listed on UCMR 3



# Non-DW Aqueous Samples

## SW-846 Method 8327 (Prep Method 3512)-Direct Injection

- Validated for groundwater, surface water, wastewater effluent
- 24 PFAS
- Based on EPA Region 5 Laboratory SOP. Similar to American Society for Testing and Materials Method D7979
- Target Quantitation Limits: 10 ng/L
- <https://www.epa.gov/hw-sw846/validated-test-method-8327-and-polyfluoroalkyl-substances-pfas-using-external-standard>





# Non-DW Aqueous Samples and Solids

## Clean Water Act Draft Method 1633

- Single-laboratory validated draft method release August 2021
- Solid phase extraction-isotope dilution
- 40 PFAS
  - All analytes listed for 533 and 537.1 plus: PFNS, PFDS, PFDoS, PFOSA, NMeFOSA, NEtFOSA, NMeFOSE, NEtFOSE, 3:3 FTCA, 5:3 FTCA, and 7:3 FTCA
- Validated for wastewater, surface water, soil, sediment, biosolids, animal tissues
- Multi-laboratory validation data collection targeted for the end of 2021
- [https://www.epa.gov/system/files/documents/2021-09/method\\_1633\\_draft\\_aug-2021.pdf](https://www.epa.gov/system/files/documents/2021-09/method_1633_draft_aug-2021.pdf)



# Total/Absorbable Organic Fluorine

Clean Water Act Method for single and multi laboratory validation

- Sorption (carbon), inorganic F<sup>-</sup> removal, combustion ion chromatography
- Delivery of draft wastewater screening method to EPA Office of Water by October 2021
- Method developed for wastewater analyses



# Total Oxidizable Precursors

Targeted method to estimate oxidizable PFAS precursors

Heated oxidative conversion

60 mM Persulfate, 125 mM Base

Oxidizable PFAA Precursors  PFCAs  
85 °C for 6 Hrs

**Total Oxidizable Precursors = PFCAs<sub>after oxidation</sub> – PFCAs<sub>before oxidation</sub>**

- Developed by Houtz et al. No multi-laboratory validated standard methods
- Available from some contract laboratories
- May not identify some precursor compounds

## Other Test Method (OTM)-45

- OTM-45 is a method for measuring 50 PFAS in air emissions from stationary sources.
- OTM-45 is a draft method that is under evaluation and will be updated and revised as data from stakeholders becomes available.
- [https://www.epa.gov/sites/default/files/2021-01/documents/otm\\_45\\_semivolatile\\_pfas\\_1-13-21.pdf](https://www.epa.gov/sites/default/files/2021-01/documents/otm_45_semivolatile_pfas_1-13-21.pdf)
- EPA is currently refining methods to characterize PFAS in emissions from stationary sources. Candidate methods for evaluation and validation expected in 2022.



## Questions?

For more information on sampling, EPA analytical methods, and links to other Federal Agency Methods see:

<https://www.epa.gov/water-research/pfas-analytical-methods-development-and-sampling-research>